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# CASE

Catalysis for Sustainable Energy

## Ni-Ga intermetallic compounds as novel catalysts for CO<sub>2</sub> hydrogenation to methanol

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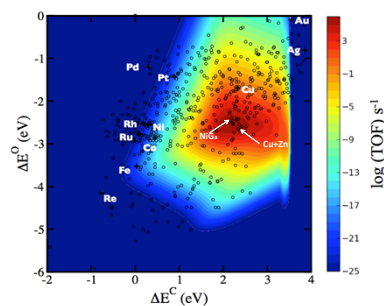
### Introduction and motivation

Synthesis of methanol from syngas (a mixture of carbon monoxide and hydrogen with small amounts of carbon dioxide) in an industrial scale is carried out at elevated temperatures and pressures (up to 250°C and 60 bar respectively), which requires high operational and investment costs.

Synthesis of methanol from synthesis gas at lower temperature and pressure are desirable if methanol is to be synthesized as a sustainable fuel in decentralized units following biomass gasification or synthesis gas production by electrolysis.

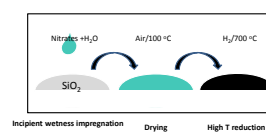
DFT enables computational identification of potential catalysts for methanol synthesis based on the optimal binding energies of the intermediate species to the surface. In the present case, binding energies of carbon and oxygen were used as descriptors.

### DFT (Density Functional Theory) calculations

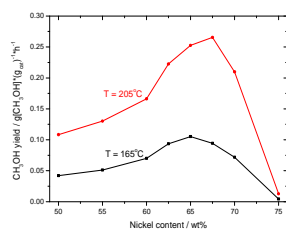
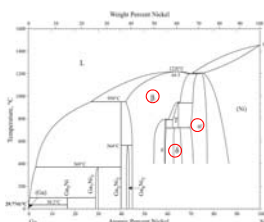


### Catalyst preparation

- A mixed aqueous solution of nickel and gallium nitrates was impregnated on high surface area silica (incipient wetness impregnation)
- Precursor dried and aged in air for 24 hours at 100-120°C
- Reduced in pure hydrogen flow for 2 hours at 700°C to form the Ni-Ga alloy.
- For comparison, a conventional Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst was synthesised following optimized co-precipitation method [1].

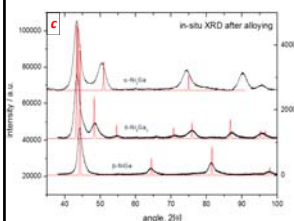
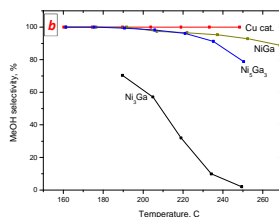
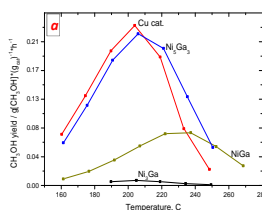


### Identifying optimal Ni/Ga ratio in the alloy



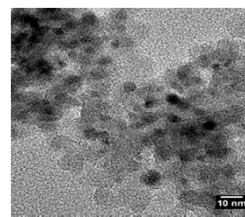
- A range of alloys with varying Ni/Ga ratio was prepared (metal loading: 17 wt%)
- Reaction conditions: 25% CO<sub>2</sub> and 75% H<sub>2</sub>, P = 1 bar
- Activity measurements revealed maximum CH<sub>3</sub>OH yield corresponding to δ-phase (Ni = 62 ± 68 mol. %)
- Ex-situ X-Ray Diffraction showed that α', β, and δ phases were formed, corresponding to Ni/Ga ratio in the impregnation mixture (Ni-Ga phase diagram taken from [2])

### Further insight into SiO<sub>2</sub>-supported β-NiGa, δ-Ni<sub>2</sub>Ga<sub>3</sub> and α'-Ni<sub>3</sub>Ga catalysts

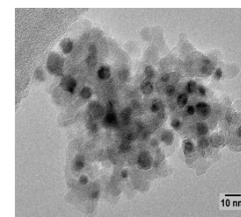


- At atmospheric pressure (a), methanol yield from Ni<sub>3</sub>Ga<sub>3</sub>/SiO<sub>2</sub> system is comparable to a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst
- Ni<sub>3</sub>Ga<sub>3</sub> composition is close to the optimal in terms of activity
- High quality XRD scans (c) confirmed the formation of targeted phases [3]
- X-Ray Fluorescence confirmed adequate Ni/Ga ratio both before and after reduction/reaction cycle

### Transmission Electron Microscopy analysis



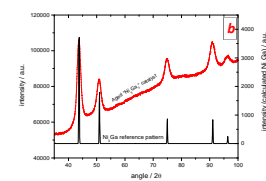
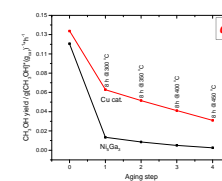
Ni<sub>3</sub>Ga<sub>3</sub>/SiO<sub>2</sub>, d = 5.1 ± 1.2 nm



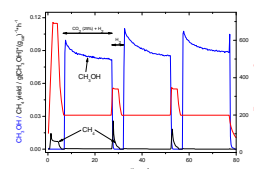
NiGa/SiO<sub>2</sub>, d = 6.2 ± 1.7 nm

- Ni-Ga intermetallic nanoparticles with narrow size distribution were formed (post-run analysis)
- Complementary to XRF data, Energy Dispersive Spectroscopy both on single particle and large area confirmed that correct Ni/Ga ratio was achieved

### Stability of the Ni<sub>3</sub>Ga<sub>3</sub>/SiO<sub>2</sub> catalyst



- Stability test in a fixed bed reactor (a) consisted of several activity testing/aging cycles. Aging temperature was increased from 300°C to 450°C with steps of 50°C. The gas mixture employed was 25% CO<sub>2</sub> and 75% H<sub>2</sub>. Activity was measured at 180°C after each aging step
- Ni<sub>3</sub>Ga<sub>3</sub> phase transformed into Ni<sub>3</sub>Ga due to de-alloying (b) at high temperatures under reaction conditions



- Catalyst is deactivated under reaction conditions but fully regenerated at 350°C in pure H<sub>2</sub> flow
- The activation energy for methane formation during regeneration (E<sub>a</sub> = 64.7 kJ/mol) correlates with α-carbon hydrogenation [4] (atomic carbon formed due to CO dissociation, E<sub>a</sub> = 70 kJ/mol)

### References

- [1] - C. Balle, Journal of Catalysis, 258, 334-344 (2008)
- [2] - H. Okamoto, Journal of Phase Equilibria and Diffusion, 31, 6, 575-576 (2010)
- [3] - Inorganic Crystal Structure Database (<http://www.fiz.karlsruhe.de/csd.html>)
- [4] - C. Bartholomew, Applied Catalysis A: General 212, 17-60 (2001)

### Acknowledgements

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